ON THE METHOD OF GROWING ALKALI

HALIDE CRYSTALS FROM A MELT

~ USSR ~

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/ Following is a translation of an article by
V. D. Kuchin which appeared in Izvestiya Vys-
shikh Uchebnykh Zavedeniy, Fizika (Proceedings
of the Higher Educational Institutions, Physics),
No. 2, Tomsk, 1958, pages 117-120._/

Starting with the value of the temperature gradient
in a crystal not greater than 10 degrees per centimeter, the
rate of cooling for NaCl crystals was found to be 2.4 degrees
per minute, for KCl - 2.32 degrees per minute, for KBr -
2.25 degrees per minute and for KI - 2.12 degrees per minu-
te. The calculated results are well supported by experi-
ments.

In the mass production of samples from crystals grown
from a melt /1/, it was noticed that in the cleavage of al-
kali-halogen crystals in the direction of (100) very often the
splitting surface so obtained was not plane-parallel, but
wave-like. It can be assumed that in the grown alkali-halo-
gen crystals, as well as in metals and semiconductors (3),
the deformation of crystals was caused by thermal stresses due
to their uneven or extremely rapid cooling.

We shall consider the thermal state of the sodium
chloride crystal grown from a melt. The heat, imparted to the
crystal by fusion is partly removed by the cooling water and
partly dissipated as radiation to the surrounding medium. We
shall find the radial and axial temperature changes in the
crystal. The heat transfer equation for the crystal having
the form of a round cylinder of radius r in cylindrical coor-
dinates, is written in the form (2)

$$\frac{\partial^2 T}{\partial \rho^2} + \frac{1}{\rho} \frac{\partial T}{\partial \rho} + \frac{\partial^2 T}{\partial z^2} = 0, \tag{1}$$

where ρ - is the flowing radius vector, z - is the ordinate.
The limiting conditions for the solution of this equation are

as follows:

1) When $z = 0$, the crystal temperature is equal to the fusion temperature.

2) The amount of heat supplied to the crystal at the expense of heat transfer from the fusion is equal to the amount of heat dissipated by the crystal surface:

$$K \frac{\partial T}{\partial \rho} = \lambda T, \qquad (2)$$

where K - is the coefficient of heat transfer, and λ - is the coefficient of heat emission. The solution of equation (1) with some approximations will assume the form (3)

$$T \cong \left(1 - \frac{\rho^2}{2r} \cdot \frac{\lambda}{K} \right) \frac{T_n}{e^{z \sqrt{\frac{2}{r} \cdot \frac{\lambda}{K}}}}. \qquad (3)$$

The given equation permits one to determine the temperature at any point in the crystal. The analysis of equation (4) shows that the temperature distribution in the crystal conforms to the exponential rule in the direction of the axes, and to the parabolic rule in the radial direction of the axes.
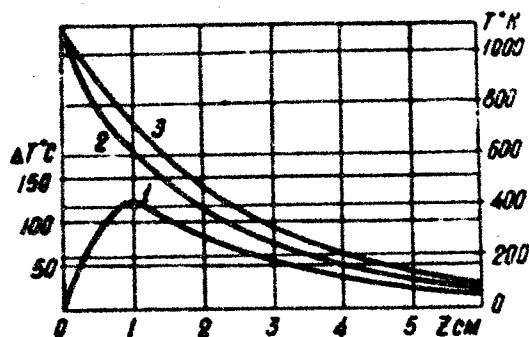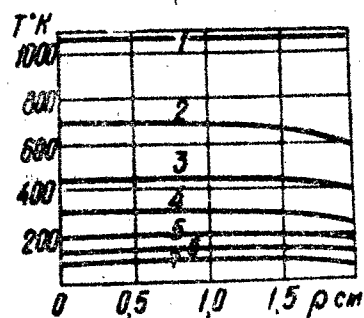

Fig. 1. Axial distribution of temperature in a crystal of NaCl grown from a melt.

Figures 1 and 2 represent the results of calculations of the respective axial and radial distribution of temperature in the NaCl crystal with the assumption that r = 2 centimeter, λ = 1 kilocalorie /centimeter/second/ degree (4), and K = 240 x 10^{-5} kilojoule/meter/second/degree (4). As can be seen from Fig. 1, the maximum temperature difference in the crystal in the radial setting takes place when z = r/2 = 1 centimeter and reaches $\Delta T = 124^\circ C$. Moreover, the value of the

$1 - z = 0,\ 2 - z = 1,\ 3 - z = 2,$
$4 - z = 3,\ 5 - z = 4,\ 6 - z = 5,$
$7 - z = 6.$

Fig. 2. Radial distribution of temperature in a crystal of NaCl grown from a melt.

calculated temperature in the center of the crystal is equal to 716°K, and at the surface of the very same crystal the temperature is equal to 592°K.

The temperature gradient in the crystal is determined according to formula (3)

$$\frac{dT}{d\rho} = \frac{\sigma}{K} T^4, \tag{4}$$

where σ is the Stephan-Boltzman constant. The calculation shows that when $z = r/2 = 1$ centimeter, the temperature gradient is equal to 314 degrees per centimeter at the fusion surface and falls to 42.5 degrees per centimeter at the crystal's apex. The greater the temperature gradient, the greater the value of mechanical stresses originating in the crystal under cooling. Since the temperature is dissimilar in various parts of the crystal, the mechanical stresses in diverse parts of the crystal will be unequal. The central part of the crystal will be the most "charged" region. The difference in linear dimensions of two neighboring parts of the very same crystal layer in the direction of radius r is proportional to the temperature difference between these two sections, that is $\Delta l = \alpha \Delta T$. These contractions are small, but they are, nevertheless, sufficient to cause plastic deformations of the crystal. The value of the mechanical stresses in the crystal can be determined from the expression

$$P = E \Delta l = E \alpha \Delta T, \tag{5}$$

3

where E - is the modulus of elasticity, and α - the temperature coefficient. For NaCl, E = 4.2 x 10⁵ kilograms per square centimeter (5), and α = 4 x 10⁻⁵ 1/per degree (6).

In the NaCl crystal when $\Delta T = 124°C$ the mechanical stresses amount to 20 kilograms per square millimeter, that is, they exceed its mechanical strength (according to data in /7/ the tensile strength for NaCl crystals amounts to 0.16 - 0.5 kilograms per square millimeter). Optical studies /8/ confirm the presence of mechanical stresses caused by the uneven cooling of the crystal under growth. Under the action of such significant mechanical stresses, a shift or "slippage" of certain crystal layers relative to others in the crystal facet, parallel to the surface of fusion, takes place. Defects in the crystal structure show up which are quite large in relation to perfect crystals /9/ and the density of which in the direction of radius r of the crystal is determined from the relationship /3/:

$$N = \frac{a}{a_0} \cdot \frac{\Delta T}{\Delta \rho} , \qquad (6)$$

where $\Delta T / \Delta \rho$ is the radial temperature difference. Recent optical and electrical measurements /8, 9/ confirmed the hypothesis regarding the existence of structural microfractures in deformed crystals. The lattice defects change the electron mobility thus contributing to the accumulation of a space charge which in turn influences the crystallizability of matter. For the determination of the density of these defects, we shall assume that $\Delta T / \Delta \rho$ = 10 degrees per centimeter /10, 11/. X-ray studies /12/ with NaCl have shown that there are no mechanical stresses operating when $\Delta T / \Delta \rho$ = 10 degrees per centimeter. The calculation for our case gives $N \cong 1.75 \times 10^5$ 1/square centimeter. The rise of radial temperature differences results in an increase in the number of lattice infractions. Therefore, in the growing of crystals from fusion, a significant role is played by the rate of crystal cooling during the growth process, which can be determined according to formula /3/

$$\frac{dT}{dt} \cong \frac{2K}{3cr} \cdot \frac{\Delta T}{\Delta \rho} , \qquad (7)$$

where c - is the specific heat of the crystal. For NaCl, c = 0.24 calories/gram degree /13/. The cooling of the crystal should be carried out slowly so that the radial temperature gradient be kept at a minimum. Expressing it differently, the isothermal surfaces in the crystal should be parallel to the surface of fusion. The cooling rate of the NaCl

crystal, as determined by the use of formula /6/ with $\Delta T/$ Δy = 10 degrees per centimeter amounts to dT/dt = 2.4 degrees per minute, that is, of the same order of magnitude as in /12,14/.

The crystal will grow only in case the rate of growth will be higher than its rate of cooling. It is known that the velocity v_k , with which pure crystals grow from fusion, can be determined approximately according to formula /15/

$$v_k \cong \frac{DS}{R_0 T_n} \cdot \frac{\Delta T_z}{\Delta z} . \tag{8}$$

where D is the diffusion coefficient, which for NaCl is equal to 0.14 square centimeters per second; S, the molar entropy of fusion is equal to 38 calories per mole degree, Δz is the distance in the direction of the crystal's expansion, in which the crystallization takes place (assumed to be equal to 5 x 10^{-2} centimeter /15/, R_0 is the universal gas constant, and ΔT_z - is the drop in temperature at the crystallization boundary (at the distance Δz). From Fig. 1, for Δz = 5 x 10^{-2} centimeter with $\Delta T/\Delta y$ = 10 degrees per centimeter, we find ΔT_z = 5 degrees, and the rate of growth v_k = 2.45 centimeters per second, that is, a significantly higher cooling rate.

For other alkali-halogen crystals an analogous calculation with several additional approximations can be carried out. We were unsuccessful in an attempt to determine the heat emission coefficient K of other crystals. For NaCl the value of the ratio λ/K is 0.175. 1/centimeter. This ratio, roughly speaking, will be constant, since the very same coefficients and K depend to a small extent upon temperature, and have values of the same order of magnitude. It can be assumed that the ratio of these coefficients is also equal to 0.175. 1/centimeter for the rest of the alkali-halogen crystals.

We consider that the error introduced with this assumption is small and is found to be within the limits of precision of the performed calculations. The values for the rate of cooling as obtained from calculation are as follows: for KCl - 2.32, for KBr - 2.25, and for KI - 2.12 degrees per minute.

The deduced calculation shows that the extremely rapid cooling of alkali-halogen crystals, grown from a melt, can be the cause of significant mechanical stresses and the occurrence of structural defects in crystals. The values found for crystal growth rate are supported by data of other authors

/12, 14/, and as the performed experiments demonstrate, they can be utilized in the practice of growing alkali-halogen crystals from a melt. The rate of crystal cooling obtained in the given calculations can be assumed to apply to maximum cooling and heating rates of samples from alkali-halogen crystals in the determination of temperature dependence upon electrical, mechanical, and other characteristics.

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